New Thiocarbonyl Ylides derived from 3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione; Generation and reactions

Woźnicka, M ; Rutkowska, M ; Mlostoń, Grzegorz ; Majchrzak, A ; Heimgartner, H

Abstract: The reaction of 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (1) with diazo compounds yielded spirocyclic 2,5-dihydro-1,3,4-thiadiazoles 3, which decomposed at ca. 45°C to give the corresponding thiocarbonyl ylide of type 4. In the absence of trapping agents, these thiocarbonyl ylides underwent a 1,3-dipolar electrocyclization to yield spirocyclic thiiranes 5. On the other hand, the thiocarbonyl methanide 4a was efficiently intercepted with C C, C=C, C=O, C=S, and N=N dipolarophiles leading to the [2+3] cycloadducts. A non-stereoselective cycloaddition took place when 3a was decomposed in the presence of the very electron-deficient dicyanofumarate or maleate, indicating a two step mechanism via an intermediate zwitterion. Furthermore, the thiocarbonyl methanide 4a could be trapped by the imidazole-2-thione 7 to give the 1,3-adduct 8. Treatment of 3a with secondary amines led to amidrazones of type 25 via base-catalyzed ring opening and condensation reaction.

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New Thiocarbonyl Ylides Derived from 3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione; Generation and Reactions

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The reaction of 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**1**) with diazo compounds yielded spirocyclic 2,5-dihydro-1,3,4-thiadiazoles **3**, which decomposed at *ca.* 45°C to give the corresponding thiocarbonyl ylide of type **4**. In the absence of trapping agents, these thiocarbonyl ylides underwent a 1,3-dipolar electrocyclization to yield spirocyclic thiiranes **5**. On the other hand, the thiocarbonyl methanide **4a** was efficiently intercepted with C≡C, C=C, C=O, C=S, and N=N dipolarophiles leading to the [2+3] cycloadducts. A non-stereoselective cycloaddition took place when **3a** was decomposed in the presence of the very electron-deficient dicyanofumarate or maleate, indicating a two step mechanism *via* an intermediate zwitterion. Furthermore, the thiocarbonyl methanide **4a** could be trapped by the imidazole-2-thione **7** to give the 1,3-adduct **8**. Treatment of **3a** with secondary amines led to amidrazones of type **25** *via* base-catalyzed ring opening and condensation reaction.

Key words: [2+3] cycloaddition, 1,3-dipolar electrocyclization, 2,5-dihydro-1,3,4-thiadiazoles, thiocarbonyl ylides

Sterically crowded aliphatic thioketones such as adamantanethione [1], 1,1,3,3-tetramethylindane-2-thione, and 2,2,4,4-tetramethyl-3-thioxocyclobutanone [2] easily undergo a [2+3] cycloaddition with diazomethane to yield regioselectively 2,5-dihydro-1,3,4-thiadiazoles. At 40–50°C, these products eliminate smoothly N_2 to give reactive thiocarbonyl *S*-methanides, which belong to the sulfur-containing 1,3-dipoles [3,4]. The availability of thioketones is one of the limitations of the preparative application of thiocarbonyl ylides. For this reason, the recently described 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**1**) [5] seemed to be an attractive parent compound for the studies aimed at the exploration of thiocarbonyl ylides. The results of these studies are presented in this paper.

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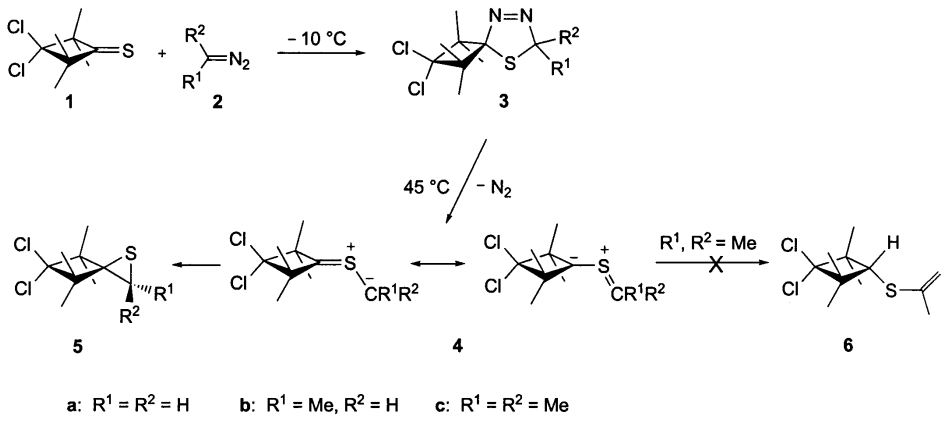
RESULTS AND DISCUSSION

Similar to other cycloaliphatic thioketones, treatment of **1** with diazomethane (**2a**) results in a fast decolorization of the solution. As the only product, the crystalline 2,5-dihydro-1,3,4-thiadiazole **3a** was obtained (Scheme 1). The ^{1}H-NMR spectrum showed the characteristic signal of the CH_2 group at 5.67 ppm; in the ^{13}C-NMR spectrum, this group resonates at 82.8 ppm. Analogous reactions with diazoethane (**2b**) and 2-diazopropane (**2c**) afforded the corresponding 2-methyl and 2,2-dimethyl derivatives (**3b** and **3c**, respectively), which could be stored in the refrigerator for several days without decomposition.

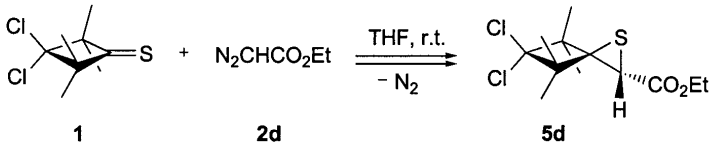
Scheme 1



When THF-solutions of the cycloadducts **3** were heated to 45°C, evolution of N_2 was observed and, after evaporation and crystallization, pure thiiranes **5a**–**c** were isolated. The reaction of **3** leading to **5** involves thiocarbonyl *S*-methanides of type **4** which in the absence of any interception reagent spontaneously undergo 1,3-dipolar electrocyclization. It is worth mentioning that in the case of **4c** the formation of **6** as a result of a [1,4] H-shift was not observed, in contrast to the previously reported result with 2,2,4,4-tetramethyl-3-oxocyclobutanethione *S*-dimethylmethanide [6]. This observation indicates that the cyclization of **4c** is faster then in the case of the 3-oxo derivative. A possible explanation of this difference is the lack of stabilization of the intermediate **4c** *via* a transannular interaction of the negative charge of the dipole with the C=O group [7].

The less reactive ethyl diazoacetate (**2d**) reacted with **1** at 50°C with instantaneous extrusion of N_2. The sole product which was obtained was the spirocyclic thiirane carboxylate **5d** (Scheme 2).

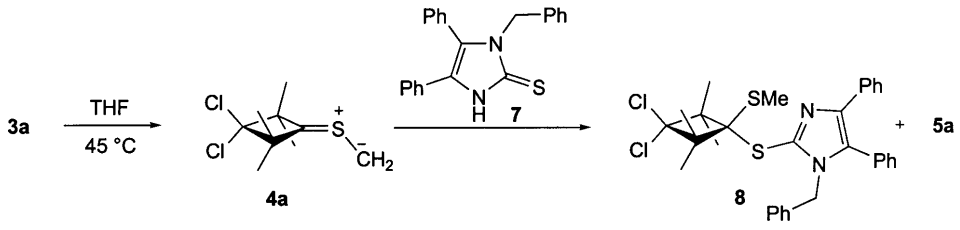
Scheme 2



1 **2d** **5d**

Reactive thiocarbonyl ylides can be intercepted either by reagents containing SH, OH or acidic NH groups or by electron deficient dipolarophiles [3,4]. Thus, the generation of **4a** by thermolysis of **3a** in THF solution in the presence of an equimolar amount of 1-benzyl-4,5-diphenylimidazole-2(3*H*)-thione (**7**) afforded a mixture of thiirane **5a** and the expected adduct **8** (Scheme 3) in a 1:1.6 ratio. Again the 1,3-dipolar electrocyclization to give **5a** competes effectively with the trapping reaction.

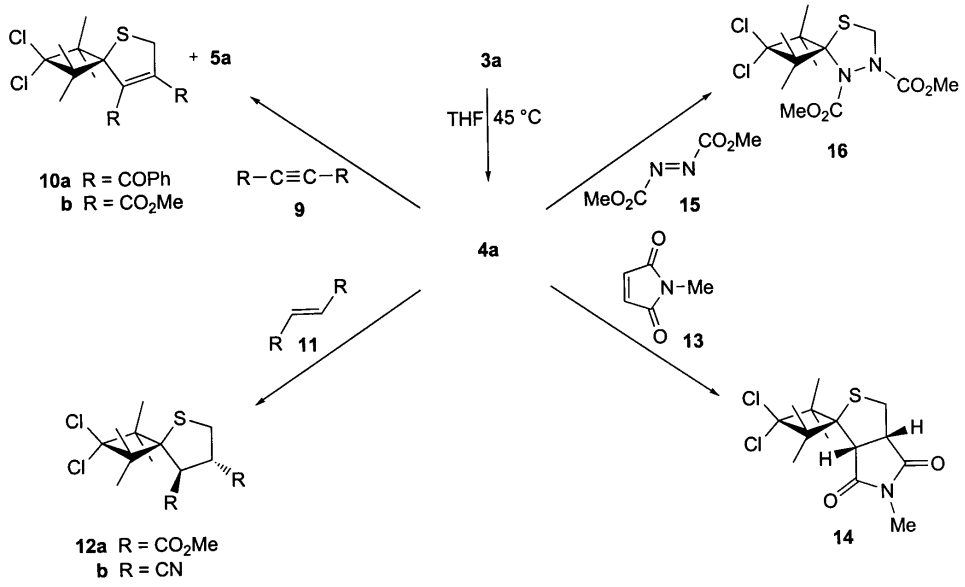
Scheme 3



4a **8**

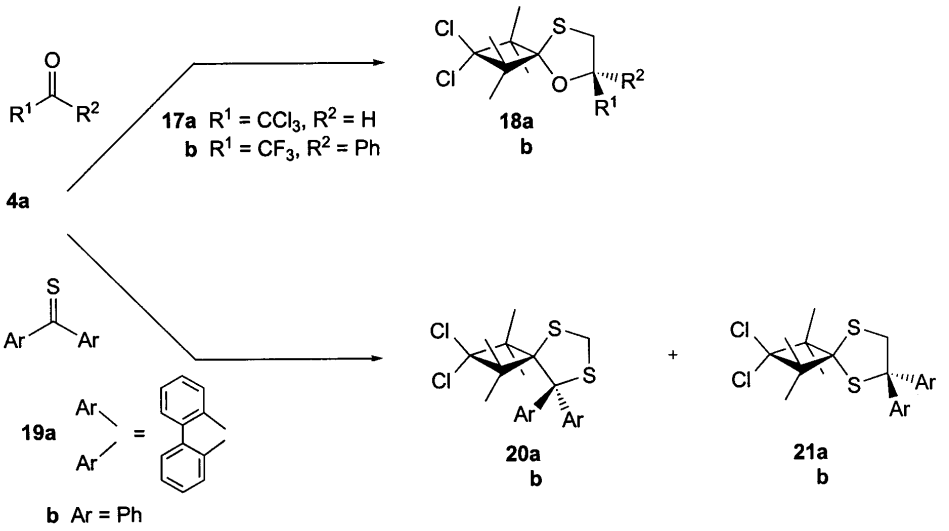
The [2+3] cycloadditions of thiocarbonyl ylides with C,C-dipolarophiles yield the corresponding di- or tetrahydrothiophene derivatives. Whereas the reaction of **4a** with dibenzoylacetylene (**9**) yielded the cycloadduct **10a** as the major product, the analogous product **10b** with dimethyl acetylene dicarboxylate was formed only in low yield (6%) in addtion to **5a** as the main product (Scheme 4). Ethylene dipolarophiles such as dimethyl fumarate (**11a**), fumaronitrile (**11b**), and *N*-methylmaleimide (**13**) reacted smoothly with **4a** to give the *trans*-substituted adducts **12a**,**b** and the *cis*-configured **14**, respectively. In contrast, the less reactive dipolarophiles dimethyl maleate and methyl acrylate [8] were not able to trap **4a**, and only thiirane **5a** was formed. On the other hand the N=N dipolarophile **15** is known as a very efficient trapping reagent for thiocarbonyl ylides [9] and, therefore, **16** was formed exclusively (Scheme 4).

Scheme 4



Electron-deficient C=O dipolarophiles used in the present study were chloral (**17a**) and trifluoroacetophenone (**17b**), and both yielded 1,3-oxathiolanes **18** (Scheme 5) in a regioselective manner. Aromatic thioketones as superior interceptors ('superdipolarophiles') reacted with **4a** to give two regioisomeric 1,3-dithiolanes **20** and **21** in favor of the sterically more congested **20** (Scheme 5).

Scheme 5



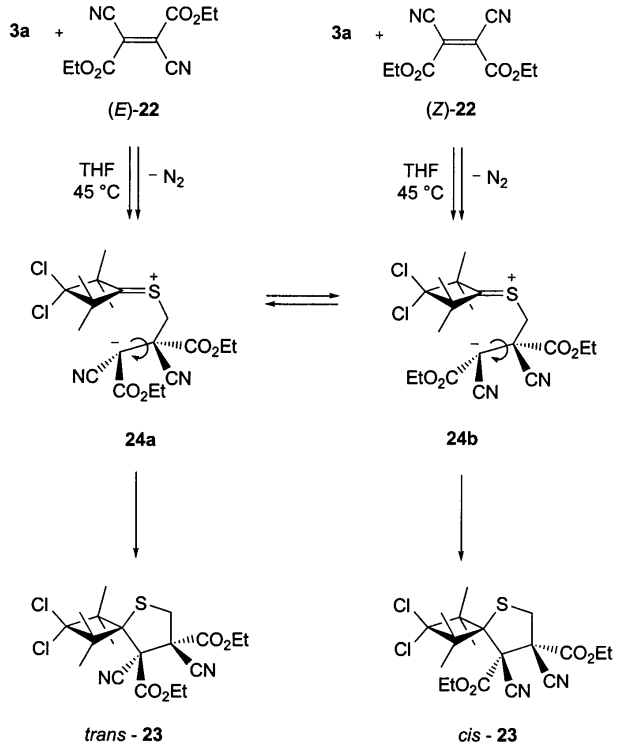
The structure of the major product was established on the basis of the ^{13}C-NMR data: the characteristic signal of CH_2 in **20a** (a '2-CH_2 1,3-dithiolane' [10,11]) appears at 29.6 ppm. The ^{1}H-NMR absorption of the CH_2 groups of **20a** and **21a** are located at 4.05 and 3.35 ppm, respectively, in accordance with previously described analogues. Thus, the ratio of the formed 1,3-dithiolanes is in agreement with the reactions described for aromatic thioketones and thiocarbonyl *S*-methanides which are structurally related to **4a** [11]. In general, the sterically more hindered '2-CH_2 1,3-dithiolane', formed *via* a 1,5-diradical intermediate, is the major product.

The reactions of electron-rich and sterically hindered thiocarbonyl *S*-methanides with electron-deficient C,C-dipolarophiles showed that formal [2+3] cycloadducts can be formed by a stepwise reaction mechanism *via* zwitterionic intermediates [12–14]. One crucial criterion is the formation of stereoisomeric cycloadducts in the reaction with stereochemically pure dipolarophiles. The relatively easily available dicyanofumarates and dicyanomaleates have been shown to act as very reactive dipolarophiles, which allow to examine the stereochemical course of the cycloaddition [13]. The reaction of **4a** with diethyl dicyanofumarate (*E*-(**22**)) occurred without formation of thiirane **5a**, and the presence of two AB-systems between 4.0 and 3.2 ppm indicated that two tetrahydrothiophenes *cis*-**23** and *trans*-**23** (Scheme 6) have been formed in a ratio of *ca.* 1:1. Fractional crystallization gave one of the cycloadducts in pure form. The comparison of its ^{1}H-NMR data with those reported for analogous products [13] allowed to identify this cycloadduct as *trans*-**23** (CH_2 appears as AB system with $\delta = 3.51$ and 3.59, $J_{AB} = 11.4$ Hz). The *cis*-isomer was isolated from the mother liquor in *ca.* 85% purity (AB system with $\delta = 3.43$ and 3.76, $J_{AB} = 13.5$ Hz). The same mixture of *trans*-**23** and *cis*-**23** was obtained when (*Z*)-**22** was used for the reaction with **3a**.

The formation of the same mixture of two stereoisomeric products *trans*- and *cis*-**23** from (*E*)-**22** as well as from (*Z*)-**22** is a clear evidence for the two-step mechanism analogous to that reported previously [13]. The initially formed zwitterionic intermediate **24a** exists in an equilibrium with **24b**, and the 1:1 ratio of *trans*-and *cis*-**23** indicates that **24a** and **24b** equilibrate completely before the ring closure takes place, *i.e.*, the ring closure is slower than the rotation about the C,C bond in the zwitterion. It is worth mentioning that in none of the hitherto reported systems the stereochemical information was completely lost [15]. The equal amounts of the tetrahydrothiophenes *trans*- and *cis*-**23** shows that the replacement of C=O by CCl_2 in the cyclobutane remarkably changes the properties of the corresponding thiocarbonyl *S*-methanides.

The 2,5-dihydro-1,3,4-thiadiazole derivatives obtained from diazomethane and thiocarbonyl compounds have been shown to react with amines *via* deprotonation. Depending on the substitution pattern, the reaction with morpholine leads to aromatic 1,3,4-thiadiazoles by elimination [16] (see also [17]) or to morpholin-4-carbaldehydhydrazones by a ring opening process and subsequent condensation with the amine [18]. The reaction of **3a** with excess of morpholine or piperidine at room temperature occurred smoothly to give the expected products **25** (Scheme 7).

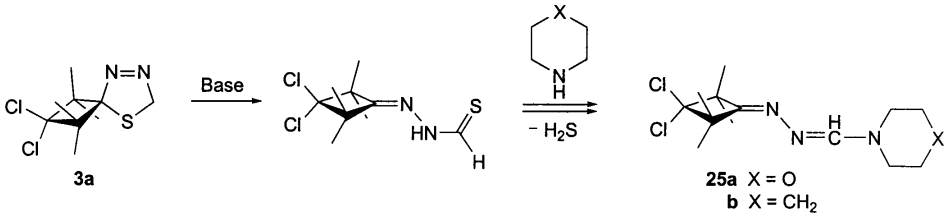
Scheme 6



Whereas the IR spectra showed only one C=N absorption at 1606 (**25a**) and 1598 (**25b**) cm^{-1}, respectively, two C=N signals were observed in the ^{13}C-NMR spectra of each compound, *e.g.* at 171.0 and 159.2 ppm for **25a**.

In summary, the chlorinated cyclobutanethione **1** is an additional useful model for reactions with the thiocarbonyl group. Its reactions with diazo compounds proceed similarly to those of other cycloaliphatic thioketones to give 2,5-dihydro-1,3,4-thiadiazoles **3**. The latter undergoes ring opening reactions by treatment with bases or eliminate N_2 when heated to 40–50°C. This thermal decomposition leads to reactive thiocarbonyl ylides **4**, which show significantly different properties in comparison with analogous species. The difference in the reaction course with dicyanofumarates are of special interest.

Scheme 7



EXPERIMENTAL

1. General. See [19]. M.p˜s were determined in capillary using a Meltemp 2 apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were registered with a Tesla BS 687 (80 MHz and 20 MHz, respectively) or a Bruker 300 (300 MHz and 75 MHz, respectively) spectrometer using TMS ($\delta_{TMS} = 0$) as an internal standard. The multiplicity of signals were elucidated based on the DEPT experiments. IR spectra were registered with a Nexus spectrophotometer (in KBr). MS (EI or CI) were recorded using a Finnigan-Mat-90 or Finnigan-SSQ-700 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the University of Zurich and the Laboratory of the Polish Academy of Sciences (CBMiM) in Łódź.

2. Starting materials. 3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione (**1**) was prepared from 3,3-dichloro-2,2,4,4-tetramethylcyclobutanone by thionation using P_4S_{10} in pyridine solution [5]. Diazomethane (**2a**) and diazoethane (**2b**) were prepared from *N*-nitroso-*N*-methylurea and *N*-nitroso-*N*-ethylurea, respectively [20]. 2-Diazopropane (**2c**) was prepared by oxidation of acetone hydrazone with yellow mercury oxide according to a known protocol [21].

3. Reaction of thione 1 with diazomethane, diazoethane and 2-diazopropane. – General procedure. A solution of thione **1 (**211 mg, 1 mmol) in a small amount of petroleum ether (or diethyl ether) was stirred magnetically in an ice bath. Solutions of diazomethane, diazoethane or 2-diazopropane, respectively, were added dropwise until decolorization of the solution was complete. After partial evaporation of the solvent, crystalline products were obtained from the solutions cooled in dry ice.

2,2-Dichloro-1,1,3,3-tetramethyl-8-thia-5,6-diazaspiro[3.4]oct-5-ene (**3a**). Yield: 190 mg (75%), colorless crystals, decomposed violently after warming to *ca.* 50°C with evolution of N_2. IR (KBr): 3007*s*, 2973*s*, 2956*s*, 2937*s*, 1578*s*, 1470*s*, 1443*s*, 1414*s*, 1385*s*, 1373*s*, 1239*s*, 976*s*, 905*vs*, 864*s*, 805*vs*, 791*s*. ^{1}H-NMR ($CDCl_3$): 1.23 (*s*, 2 Me), 1.44 (*s*, 2 Me), 5.67 (*s*, CH_2). ^{13}C-NMR ($CDCl_3$): 22.1 (2 Me), 27.8 (2 Me), 58.5 (2 C_q), 82.8 (CH_2), 99.7 (CCl_2), 118.0 (NC_qS).

2,2-Dichloro-1,1,3,3,7-pentamethyl-8-thia-5,6-diazaspiro[3.4]oct-5-ene (**3b**). Yield: 221 mg (83%), colorless crystals, m. p. 52–59°C (diethyl ether). IR (KBr): 2980*m*, 1469*m*, 1445*m*, 1383*m*, 1372*m*, 904*vs*, 809*s*. ^{1}H-NMR ($CDCl_3$): 1.22 (*s*, Me), 1.26 (*s*, Me), 1.43 (*s*, 2 Me), 1.69 (*d*, $J_{H,H}$ = 6.4, Me), 5.92 (*q*, $J_{H,H}$ = 6.4, CH). ^{13}C-NMR ($CDCl_3$): 21.5, 21.8, 21.9 (4 Me), 27.7 (Me), 57.9, 58.1 (2 C_q), 93.3 (CH), 99.3 (CCl_2), 117.4 (NC_qS).

2,2-Dichloro-1,1,3,3,7,7-hexamethyl-8-thia-5,6-diazaspiro[3.4]oct-5-ene (**3c**). Yield: 98 mg (35%), colorless crystals, m. p. 21–24°C (diethyl ether). IR (KBr): 2978*s*, 2927*m*, 1469*s*, 1454*s*, 1382*s*, 1369*m*, 901*vs*, 833*s*, 807*s*. ^{1}H-NMR ($CDCl_3$): 1.23 (*s*, 2 Me), 1.39 (*s*, 2 Me), 1.67 (*s*, 2 Me). ^{13}C-NMR ($CDCl_3$): 22.0 (2 Me), 28.0 (2 Me), 29.9 (2 Me), 58.3 (2 C_q), 99.8 (CCl_2), 104.2 (Me_2C_q), 117.9 (NC_qS).

4. Thermal decomposition of 2,5-dihydro-1,3,4-thiadiazoles 3. – General procedure. A solution of 1 mmol of the corresponding 2,5-dihydro-1,3,4-thiadiazole **3** in 2 ml of abs. THF was magnetically stirred and heated in an oil bath at 45°C (**3a** and **3b**) or in 2 ml of xylene at 70°C (**3c**). The N_2 evolution was controlled using a gas-burette and the reaction vessel was heated until the evolution of the gas ceased (*ca.* 3 h). Then, the solvent was evaporated and the product was purified by crystallization from methanol.

5,5-Dichloro-4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexane (**5a**). Yield: 130 mg (58%), colorless crystals, m. p. 204–207°C (methanol). IR (KBr): 2986*m*, 2974*m*, 913*s*, 826*s*, 797*s*. ^{1}H-NMR ($CDCl_3$): 1.31 (*s*, 2 Me), 1.55 (*s*, 2 Me), 2.63 (*s*, CH_2). ^{13}C-NMR ($CDCl_3$): 23.6 (2 Me), 26.2 (CH_2), 28.5 (2 Me), 54.0 (2 C_q), 62.0 (C_qS), 98.8 (CCl_2). EI-MS: 209 (38), 191 (36), 189 (100, [*M*-Cl]$^+$), 100 (52), 85 (88). Anal. Calc. for $C_9H_{14}Cl_2S$ (225.18): C 48.01, H 6.27, S 14.24. Found: C 48.03, H 6.33, S 14.31.

5,5-Dichloro-2,4,4,6,6-pentamethyl-1-thiaspiro[2.3]hexane (**5b**). Yield: 135 mg (56%), colorless crystals, m. p. 148–152°C (methanol). IR (KBr): 2993*m*, 2972*m*, 1466*m*, 1369*m*, 904*s*, 821*s*. ^{1}H-NMR ($CDCl_3$): 1.19, 1.34, 1.37, 1.50 (4*s*, 4 Me), 1.57 (*d*, $J_{H,H}$ = 6.2, Me), 2.99 (*q*, $J_{H,H}$ = 6.2, CH). ^{13}C-NMR ($CDCl_3$): 20.8, 25.0, 25.7, 27.3, 29.6 (5 Me), 38.0 (CH), 53.9, 54.8 (2 C_q), 67.3 (C_qS), 99.9 (CCl_2). CI-MS: 241 (35), 239 (51, $M^{+\cdot}$), 205 (35), 203 (100, [*M*-Cl]$^+$), 114 (58). Anal. Calc. for $C_{10}H_{16}Cl_2S$ (239.21): C 50.21, H 6.74. Found: C 50.03, H 6.23.

5,5-Dichloro-2,2,4,4,6,6-hexamethyl-1-thiaspiro[2.3]hexane (**5c**). Yield: 143 mg (57%), colorless crystals, m. p. 157–160°C (methanol). IR (KBr): 3008*m*, 2992*m*, 2964*m*, 1456*m*, 1372*s*, 1095*m*, 923*m*, 886*m*, 811*s*. ^{1}H-NMR ($CDCl_3$): 1.26 (*s*, 2 Me), 1.61 (*s*, 2 Me), 1.64 (*s*, 2 Me). ^{13}C-NMR ($CDCl_3$): 25.7 (2 Me), 28.2 (2 Me), 28.4 (2 Me), 49.0 (Me_2C_q), 55.0 (2 C_q), 72.5 (C_qS), 100.7 (CCl_2). CI-MS: 257 (14),

255 (70), 254 (18), 253 (100, $M^{+\cdot}$), 217 (10, [M-Cl]$^+$). Anal. Calc. for $C_{11}H_{18}Cl_2S$ (253.24): C 52.17, H 7.16. Found: C 51.79, H 6.40.

5. Reaction of 1 with ethyl diazoacetate. A solution of 211 mg (1 mmol) of **1** and 114 mg (1 mmol) of ethyl diazoacetate in 1 ml chloroform was stirred magnetically at room temperature for *ca*. 20 h (until evolution of N_2 ceased). The product was isolated by preparative layer chromatography (SiO_2, CH_2Cl_2) and an analytically pure sample was obtained by crystallization from methanol.

Ethyl 5,5-dichloro-4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexane-2-carboxylate (**5d**). Yield: 272 mg (92%), colorless crystals, m. p. 25–28°C (methanol). IR (KBr): 1747*s* (C=O), 1725*m*, 1371*m*, 1178*s*, 915*m*, 825*m*. ^{1}H-NMR ($CDCl_3$): 1.17 (*s*, Me), 1.31 (*t*, $J_{H,H}$ = 7.1, *Me*CH_2), 1.40 (*s*, 2 Me), 1.45 (*s*, Me), 3.29 (*s*, CH), 4.22 (*q*, $J_{H,H}$ = 7.1, Me*CH*$_2$). ^{13}C-NMR ($CDCl_3$): 14.0 (*Me*CH_2), 24.5, 26.3, 26.9, 28.1 (4 Me), 36.5 (CH), 54.7, 55.1 (2 C_q), 62.2 (Me*C*H_2), 67.6 (C_qS), 99.8 (CCl_2), 169.0 (CO). CI-MS: 316 (69), 314 (100, [M+NH_3]$^+$), 297 (15, $M^{+\cdot}$), 261 (19, [M-Cl]$^+$), 172 (17). Anal. Calc. for $C_{12}H_{18}O_2Cl_2S$ (297.25): C 48.49, H 6.10, S 10.79. Found: C 48.36, H 5.95, S 10.99.

6. Decomposition of 3a in the presence of imidazole-2-tione 7 or a dipolarophile. A solution containing 253 mg (1 mmol) **3a** and 1 mmol of the corresponding interception reagent in 2 ml of dry THF was magnetically stirred and heated in the oil bath at 45°C until the evolution of N_2 ceased (*ca*. 3 h). The solvent was evaporated and the product was isolated either by preparative thin layer chromatography using plates precoated with SiO_2 or by crystallization.

1-Benzyl-2-[3,3-dichloro-2,2,4,4-tetramethyl-1-(methylsulfanyl)cyclobutylsulfanyl]-4,5-diphenyl-1H-imidazole (**8**). Yield: 162 mg (29%), colorless crystals, m. p. 183–188°C (CH_2Cl_2/petroleum ether). IR (KBr): 1450m, 1443m, 766m, 702s. ^{1}H-NMR ($CDCl_3$): 1.62 (*s*, 2 Me), 1.88 (*s*, 2 Me), 2.07 (*s*, MeS), 5.07 (*s*, CH_2), 6.71–7.60 (*m*, 15 CH_{arom}). ^{13}C-NMR ($CDCl_3$): 16.3 (CH_2), 24.7 (2 Me), 28.4 (2 Me), 48.4 (2 C_q), 59.1 (MeS), 77.9 (C_qS_2), 101.1 (CCl_2), 126.7, 127.8, 128.4, 128.9, 129.2, 130.9, 131.4, 131.5, 134.9, 137.6, 139.7 (21 C_{arom}). CI-MS: 569 (0.9), 567 (1, $M^{+\cdot}$), 497 (4), 451 (3), 357 (18), 312 (22), 311 (100), 227 (11), 225 (16). ESI-MS (MeOH/CH_2Cl_2, NaI): 589 (100, [M+Na]$^+$). Anal. Calc. for $C_{31}H_{32}Cl_2N_2S_2$ (567.65): C 65.59, H 5.68, N 4.94, S 12.49. Found: C 65.61, H 5.50, N 4.74, S 12.49.

(7-Benzoyl-2,2-dichloro-1,1,3,3-tetramethyl-5-thiaspiro[3.4]oct-7-en-8-yl)phenylmethanone (**10a**). Yield: 81 mg (18%), yellow crystals, m. p. 213–215°C (CH_2Cl_2/methanol). IR (KBr): 1665*vs* (C=O), 1651*s* (C=O), 1594*m*, 1449*m*, 1295*m*, 1260*m*, 702*s*. ^{1}H-NMR ($CDCl_3$): 1.54 (*s*, 2 Me), 1.58 (*s*, 2 Me), 3.90 (*s*, CH_2), 7.26–7.36, 7.42–7.53, 7.63–7.66 (3*m*, 10 CH_{arom}). ^{13}C-NMR ($CDCl_3$): 27.0 (2 Me), 27.4 (2 Me), 37.3 (CH_2), 58.2 (2 C_q), 80.4 (C_qS), 100.0 (CCl_2), 128.2, 128.4, 129.0, 129.4, 133.5, 133.6 (10 CH_{arom}), 136.4, 138.2, 146.0, 149.1 (4 C_q), 193.0, 194.9 (2 CO). CI-MS: 478 (69), 476 (98, [M+NH_3]$^+$), 459 (62, $M^{+\cdot}$), 440 (100), 425 (70), 389 (88). Anal. Calc. for $C_{25}H_{24}O_2Cl_2S$ (459.44): C 65.36, H 5.27, Cl 15.43, S 6.98. Found: C 64.89, H 5.21, Cl 15.18, S 5.87.

Dimethyl 2,2-dichloro-1,1,3,3-tetramethyl-5-thiaspiro[3.4]oct-7-ene-7,8-dicarboxylate (**10b**). Yield: 32 mg (8%), colorless crystals, m. p. 65–68°C (hexane). IR (KBr): 1743*s* (C=O), 1717*s* (C=O), 1440*m*, 1303*s*, 1258*s*, 1225*m*, 1205*s*, 1145*m*, 811*m*. ^{1}H-NMR ($CDCl_3$): 1.48 (*s*, 2 Me), 1.57 (*s*, 2 Me), 3.66 (CH_2), 3.75 (*s*, MeO), 3.81 (*s*, MeO).^{13}C-NMR ($CDCl_3$): 25.4 (2 Me), 27.0 (2 Me), 34.5 (CH_2), 52.3, 52.6 (2 MeO), 58.3 (2 C_q), 77.0 (C_qS), 99.8 (CCl_2), 137.4, 148.4 (2 C_q), 162.8, 167.3 (2 CO). CI-MS: 388 (15), 386 (72), 384 (100, [M+NH_3]$^+$), 331 (13, [M-Cl]$^+$). Anal. Calc. for $C_{15}H_{20}O_4Cl_2S$ (367.29): C 49.05, H 5.49, S 8.73. Found: C 48.96, H 5.72, S 8.69.

Dimethyl 2,2-dichloro-1,1,3,3-tetramethyl-5-thiaspiro[3.4]octane-7,8-dicarboxylate (**12a**). Yield: 170 mg (46%), colorless crystals, m. p. 72–74°C (hexane). IR (KBr): 1740*s* (C=O), 1433*m*, 1203*m*, 1166*m*. ^{1}H-NMR ($CDCl_3$): 1.32, 1.38, 1.46, 1.53 (4*s*, 4 Me), 3.14, 3.16 (2*s*, 2 CH), 3.73, 3.75 (2*s*, 2 MeO), 3.81 (*s*, CH_2). ^{13}C-NMR ($CDCl_3$): 24.0, 25.8, 25.9, 26.3 (4 Me), 32.8 (CH_2), 52.1, 52.4, 52.5, 53.2 (2 MeO, 2 CH), 55.0, 56.9 (2 C_q), 71.1 (C_qS), 101.1 (CCl_2), 171.7, 173.1 (2 CO). CI-MS: 388 (72), 386 (100, [M+NH_3]$^+$), 371 (54), 369 (80, $M^{+\cdot}$). Anal. Calc. for $C_{15}H_{22}O_4Cl_2S$ (369.31): C 48.78, H 6.00, S 8.68. Found: C 46.69, H 5.84, S 7.32.

2,2-Dichloro-1,1,3,3-tetramethyl-5-thiaspiro[3.4]octane-7,8-dicarbonitrile (**12b**). Yield: 127 mg (33%), colorless crystals, m. p. 144–147°C (methanol). IR (KBr): 1473*m*, 1460*m*, 1389*m*, 1373*m*, 888*m*, 814*s*. ^{1}H-NMR ($CDCl_3$): 1.44, 1.55, 1.67, 1.81 (4*s*, 4 Me), 3.13–3.18, 3.47–3.55, 3.70–3.78 (3*m*, CH_2, 2 CH). ^{13}C-NMR ($CDCl_3$): 24.5, 25.6, 25.7, 25.8 (4 Me), 33.7 (CH_2), 35.5, 42.2, (2 CH), 54.1, 56.4 (2 C_q), 71.2 (C_qS), 99.1 (CCl_2), 117.8, 118.2 (2 CN). CI-MS: 322 (72), 321 (17), 320 (100, [M+NH_3]$^+$), 178 (17).

Anal. Calc. for $C_{13}H_{16}Cl_2N_2S$ (303.26): C 51.49, H 5.32, N 9.24, S 10.57. Found: C 51.35, H 5.56, N 9.14, S 10.35.

3′,3′-Dichloro-7,2′,2′,4′,4′-pentamethyl-3-thia-7-azaspiro[bicyclo[3.3.0]octane-2,1′-cyclobutane]-6,8-dione (**14**). Yield: 136 mg (40%), colorless crystals, m. p. 174–178°C (CH_2Cl_2/hexane). IR (KBr): 1702*s* (C=O), 1436*m*, 1382*m*. ^{1}H-NMR ($CDCl_3$): 1.38, 1.48, 1.50, 1.96 (4*s*, 4 Me), 2.99 (*s*, MeN), 2.91–2.97, 3.15–3.24, 3.60–3.62 (3*m*, CH_2, 2 CH). ^{13}C-NMR ($CDCl_3$): 24.1, 25.1, 25.2, 25.8, 26.5 (5 Me), 35.3 (CH_2), 45.6 (CH), 53.3 (C_q), 53.8 (CH), 55.1 (C_q), 70.4 (C_qS), 100.0 (CCl_2), 175.2, 177.1 (2 CO). CI-MS: 369 (10), 353 (9, $[M+NH_3]^+$), 302 (9), 300 (23, $[M-Cl]^+$), 213 (11), 212 (13), 211 (100). Anal. Calc. for $C_{14}H_{19}Cl_2NO_2S$ (336.28): C 50.00, H 5.69, N 4.17, S 9.54. Found: C 49.91, H 5.66, N 4.17, S 9.38.

Dimethyl 2,2-dichloro-1,1,3,3-tetramethyl-8-thia-5,6-diazaspiro[3.4]octane-5,6-dicarboxylate (**16**) (because of different conformations there are more signals in the ^{1}H-NMR and ^{13}C-NMR spectra then expected). Yield: 184 mg (50%), colorless crystals, m. p. 136–138°C (methanol). IR (KBr): 1759*s* (C=O), 1709*vs* (C=O), 1455*s*, 1443*m*, 1389*s*, 1260*s*, 1196*m*. ^{1}H-NMR ($CDCl_3$): 1.36, 1.46, 1.53, 1.87 (4*s*, 4 Me), 3.78, 3.80, 3.81, 3.81 (4*s*, 2 MeO), 4.34–4.37, 4.53–4.61 (2*m*, CH_2). ^{13}C-NMR ($CDCl_3$): 23.6, 24.0, 24.6, 24.7, 25.6, 25.8, 26.2, 26.3 (4 Me), 49.7, 49.9 (CH_2), 53.3, 53.3, 54.3 (2 MeO), 55.8, 55.8, 58.0 (2 C_q), 88.7, 89.1 (C_qS), 98.6 (CCl_2), 152.2, 153.8, 158.0, 158.1 (2 CO). CI-MS: 392 (11), 390 (53), 389 (13), 388 (77, $[M+NH_3]^+$), 373 (13), 371 (19, $M^{+\cdot}$), 178 (100), 166 (35). Anal. Calc. for $C_{13}H_{20}Cl_2N_2O_4S$ (371.28): C 42.06, H 5.43, N 7.55, S 8.64. Found: C 41.91, H 5.77, N 7.52, S 8.50.

2,2-Dichloro-1,1,3,3-tetramethyl-6-trichloromethyl-5-oxa-8-thiaspiro[3.4]octane (**18a**). Yield: 290 mg (78%), colorless crystals, m. p. 25–26°C (diethyl ether). IR (KBr): 1470*m*, 1110*m*, 959*m*, 816*br*, 809*br*, 659*m*. ^{1}H-NMR ($CDCl_3$): 1.35, 1.37, 1.43, 1.46 (4*s*, 4 Me), 3.04–3.19 (*m*, CH_2), 4.56 (*dd*, $J_{H,H}$ = 8.9, 5.4, CH). ^{13}C-NMR ($CDCl_3$): 21.1, 21.8, 26.9, 27.6 (4 Me), 33.7 (CH_2), 58.6, 59.9 (2 C_q), 91.3 (CH), 97.4 (C_qS), 98.6 (CCl_2), 102.7 (CCl_3). CI-MS: 339 (24), 337 (47, $[M-Cl]^+$), 335 (36), 250 (36), 248 (99), 246 (100). Anal. Calc. for $C_{11}H_{15}Cl_5OS$ (372.57): C 35.46, H 4.06, S 8.61. Found: C 35.49, H 4.13, S 8.67.

2,2-Dichloro-1,1,3,3-tetramethyl-6-phenyl-6-trifluoromethyl-5-oxa-8-thiaspiro[3.4]-octane (**18b**). Yield: 183 mg (46%), colorless crystals, m. p. 57–60°C (hexane). IR (KBr): 1300*m*, 1179*vs*, 1167*vs*, 1083*m*, 1067*m*, 1016*m*, 902*m*, 768*m*, 708*s*. ^{1}H-NMR ($CDCl_3$): 1.24, 1.39, 1.44, 1.55 (4*s*, 4 Me), 3.40–3.44, 3.61–3.65 (2*m*, CH_2), 7.35–7.52 (*m*, 5 CH_{arom}). ^{13}C-NMR ($CDCl_3$): 23.5, 25.1, 25.3, 26.2 (4 Me), 38.0 (CH_2), 59.3, 59.4 (2 C_q), 89.8 (*q*, $^2J_{C,F}$ = 28.6, C_qCF_3), 98.1 (CCl_2), 105.1 (C_qS), 124.2 (*q*, $^1J_{C,F}$ = 286.6, CF_3), 127.1, 128.1, 129.0 (5 CH_{arom}), 136.2 ($C_{q\text{-}arom}$). CI-MS: 365 (12), 363 (26, $[M-Cl]^+$), 275 (25), 274 (100). Anal. Calc. for $C_{17}H_{19}Cl_2F_3OS$ (399.30): C 51.14, H 4.80, S 8.03. Found: C 50.84, H 4.97, S 8.07.

*3,3-Dichloro-2,2,4,4-tetramethyldispiro[cyclobutan-1,4′-[1.3]dithiolan-5′,9″-[9*H*]fluoren]* (**20a**). Yield: 189 mg (45%), colorless crystals, m. p. 173–178°C (CH_2Cl_2/hexane). IR (KBr): 1445*m*, 1437*m*, 1383*m*, 810*m*, 753*s*. ^{1}H-NMR ($CDCl_3$): 1.28, 1.41 (2*s*, 4 Me), 4.05 (*s*, CH_2), 7.20–7.25, 7.35–7.40, 7.64–7.67, 8.24–8.27 (4*m*, 8 CH_{arom}). ^{13}C-NMR ($CDCl_3$): 26.7, 26.9 (4 Me), 29.6 (CH_2), 60.0 (2 C_q), 73.5 (C_qS), 102.1 (CCl_2), 119.3, 126.0, 128.9, 129.9 (8 CH_{arom}), 141.2, 145.0 (4 $C_{q\text{-}arom}$). CI-MS: 438 (48, $[M+NH_3]^+$), 423 (49), 421 (64, $M^{+\cdot}$), 385 (51, $[M-Cl]^+$), 374 (46), 307 (100). Anal. Calc. for $C_{22}H_{22}Cl_2S_2$ (421.45): C 62.70, H 5.26, S 15.22. Found: C 62.66, H 5.26, S 15.31.

2,2-Dichloro-1,1,3,3-tetramethyl-8,8-diphenyl-5,7-dithiaspiro[3.4]octane (**20b**). Yield: 190 mg (45%), colorless crystals, m. p. 160–166°C (CH_2Cl_2/methanol). IR (KBr): 1494*m*, 1444*m*, 1384*m*, 812*m*, 731*s*, 706*m*, 693*s*. ^{1}H-NMR ($CDCl_3$): 1.23 (*s*, Me), 1.75 (*s*, Me), 1.85 (*s*, 2 Me), 3.08, 3.47 (*AB*, $J_{H,H}$ = 7.3, CH_2), 7.14–7.69 (*m*, 10 CH_{arom}). ^{13}C-NMR ($CDCl_3$): 26.0 (CH_2), 28.9, 29.4, 29.6 (4 Me), 58.8, 61.4 (2 C_q), 77.5 (C_qS), 79.1 (C_qS), 102.5 (CCl_2), 126.3, 126.8, 127.3, 129.1, 133.2 (10 CH_{arom}), 141.0, 147.8 (2 $C_{q\text{-}arom}$). CI-MS: 426 (20), 425 (78), 424 (27), 423 (100, $M^{+\cdot}$), 387 (26, $[M-Cl]^+$), 273 (20), 199 (36). Anal. Calc. for $C_{22}H_{24}Cl_2S_2$ (423.47): C 62.40, H 5.71. Found: C 62.72, H 5.48.

*3,3-Dichloro-2,2,4,4-tetramethyldispiro[cyclobutan-1,2′-[1.3]dithiolan-4′,9″-[9*H*]fluoren]* (**21a**). Yield: 28 mg (7%), colorless crystals, m. p. 132–136°C (CH_2Cl_2/methanol). IR (KBr): 1446*m*, 806*m*, 746*m*, 725*m*. ^{1}H-NMR ($CDCl_3$): 1.67, 1.67 (2*s*, 4 Me), 3.35 (*s*, CH_2), 7.25–7.40, 7.64–7.67, 7.82–7.85 (3*m*, 8 CH_{arom}). ^{13}C-NMR ($CDCl_3$): 25.6, 28.9 (4 Me), 51.2 (CH_2), 59.2 (2 C_q), 70.0 (C_qS), 80.6 (C_qS_2), 100.0 (CCl_2), 119.9, 124.7, 128.0, 128.6 (8 CH_{arom}), 139.1, 148.3 (4 $C_{q\text{-}arom}$). CI-MS: 440 (61), 438 (79,

[M+NH_3]$^+$), 423 (43), 421 (56, $M^{+\cdot}$), 385 (46, [M-Cl]$^+$), 296 (43), 178 (100). Anal. Calc. for $C_{22}H_{22}Cl_2S_2$ (421.45): C 62.70, H 5.26. Found: C 62.75, H 4.71.

2,2-Dichloro-1,1,3,3-tetramethyl-6,6-diphenyl-5,8-dithiaspiro[3.4]octane (**21b**). Yield: 46 mg (11%), colorless crystals, m. p. 126–134°C (CH_2Cl_2/hexane). IR (KBr): 1445*m*, 877*m*, 803*m*, 748*m*, 697*s*. ^{1}H-NMR ($CDCl_3$): 1.29, 1.48 (2*s*, 4 Me), 3.76 (*s*, CH_2), 7.19–7.31, 7.42–7.45 (2*m*, 10 CH_{arom}). ^{13}C-NMR ($CDCl_3$): 25.7, 28.1 (4 Me), 49.5 (CH_2), 59.4 (2 C_q), 73.0 (C_qS), 78.5 (C_qS_2), 100.0 (CCl_2), 127.1, 127.8, 128.1 (10 CH_{arom}), 143.8 (2 $C_{q\text{-}arom}$). CI-MS: 440 (11, [M+NH_3]$^+$), 423 (11, $M^{+\cdot}$), 389 (15), 387 (16, [M-Cl]$^+$), 298 (13), 214 (17), 213 (100), 180 (18). Anal. Calc. for $C_{22}H_{24}Cl_2S_2$ (423.47): C 62.40, H 5.71, N 15.14. Found: C 62.15, H 5.55, N 14.96.

Diethyl trans-*2,2-dichloro-7,8-dicyano-1,1,3,3-tetramethyl-5-thiaspiro[3.4]octane-7,8-dicarboxylate* (*trans*-**23**). Yield: 105 mg (23%), colorless crystals, m. p. 134–136°C (CH_2Cl_2/hexane). IR (KBr): 1755*vs* (C=O), 1389*m*, 1239*vs*, *br*, 1038*m*, 1011*m*. ^{1}H-NMR ($CDCl_3$): 1.35, 1.42 (2*t*, $J_{H,H}$ = 7.1, 2 *Me*CH_2), 1.62, 1.63, 1.72, 1.98 (4*s*, 4 Me), 3.51, 3.59 (*AB*, $J_{H,H}$ = 11.4, CH_2), 4.35, 4.40 (2*q*, $J_{H,H}$ = 7.1, 2 Me*C*H_2). ^{13}C-NMR ($CDCl_3$): 13.2, 13.7 (2 *Me*CH_2), 26.1, 26.4, 26.7, 26.9 (4 Me), 36.4 (CH_2), 58.7, 59.9, 60.7, 62.8 (4 C_q), 64.6, 64.7 (2 Me*C*H_2), 72.8 (C_qS), 100.5 (CCl_2), 114.7, 116.0 (2 CN), 163.0, 163.2 (2 CO). CI-MS: 466 (74), 465 (24), 464 (100, [M+NH_3]$^+$).

Diethyl cis-*2,2-dichloro-7,8-dicyano-1,1,3,3-tetramethyl-5-thiaspiro[3.4]octane-7,8-dicarboxylate* (*cis*-**23**). After preliminary chromatography on SiO_2-plates (hexane/CH_2Cl_2) followed by fractional crystallization from hexane/CH_2Cl_2 obtained as a 85:15 mixture with *trans*-**23**; colorless crystals, m. p. 58–65°C. ^{1}H-NMR ($CDCl_3$): 1.25, 1.76, 1.95, 2.12 (4*s*, 4 Me), 1.35, 1.38 (2*t*, $J_{H,H}$ = 7.1, 2 *Me*CH_2), 3.43, 3.76 (*AB*, $J_{H,H}$ = 12.5, CH_2), 4.32 (*q*, $J_{H,H}$ = 7.1, 2 Me*C*H_2).

7. Reactions of 3a with morpholine or piperidine. To the magnetically stirred amine (1 ml) at room temperature, 253 mg (1 mmol) of **3a** were added in small portions. Stirring was continued for *ca*. 2 h at room temperature. Then, the mixture was diluted with 25 ml of CH_2Cl_2 and washed three times with brine. The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and the filtrate was evaporated to dryness. An analytically pure sample was obtained by crystallisation from hexane.

N-*(3,3-Dichloro-2,2,4,4-tetramethylcyclobutylidene)-(*N′*-morpholin-4-yl)methylidene-hydrazine* (**25a**). Yield: 189 mg (62%), colorless crystals, m. p. 91–95°C (petroleum ether). IR (KBr): 1606*s* (C=N), 1233*m*, 1118*m*. ^{1}H-NMR ($CDCl_3$): 1.45, 1.56 (2*s*, 4 Me), 3.30–3.44, 3.63–3.77 (2*m*, 2 CH_2CH_2), 7.80 (*s*, CH). ^{13}C-NMR ($CDCl_3$): 24.4, 25.6 (4 Me), 46.5 (2 CH_2N), 58.3, 61.3 (2 C_q), 66.6 (2 CH_2O), 98.6 (CCl_2), 159.2 (CH), 171.0 (C_qN). CI-MS: 310 (11), 309 (10), 308 (64), 307 (15), 306 (100, $M^{+\cdot}$). Anal. Calc. for $C_{13}H_{21}Cl_2N_3O$ (306.24): C 50.99, H 6.91, N 13.72. Found: C 51.22, H 6.63, N 13.83.

N-*(3,3-Dichloro-2,2,4,4-tetramethylcyclobutylidene)-(*N′*-piperidin-1-yl)methylidene-hydrazine* (**25b**). Yield: 130 mg (43%), colorless crystals, m. p. 114–116°C (petroleum ether). IR (KBr): 2931*m*, 1598*vs*, 1450*m*, 1255*m*, 1213*m*, 1124*m*. ^{1}H-NMR ($CDCl_3$): 1.45, 1.58 (2*s*, 4 Me), 1.58–1.64 (*m*, $(CH_2)_3$), 3.32 (*s*, 2 CH_2N), 7.78 (s, CH). ^{13}C-NMR ($CDCl_3$): 31.9, 33.2 (4 Me), 32.2, 33.0, 33.3 (3 CH_2), 55.1 (2 CH_2N), 65.8, 68.7 (2 C_q), 106.2 (CCl_2), 166.7 (CH), 176.6 (C_qN). CI-MS: 306 (68), 305 (18), 304 (100, $M^{+\cdot}$), 268 (17, [M-Cl]$^+$). Anal. Calc. for $C_{14}H_{23}Cl_2N_3$ (304.26): C 55.27, H 7.62, N 13.81. Found: C 55.30, H 7.66, N 13.91.

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